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## DESCRIPTION



THERMOELECTRIC CONVERSION MATERIAL, THERMOELECTRIC  
CONVERSION DEVICE AND MANUFACTURING METHOD THEREOF

5

## TECHNICAL FIELD

The present invention relates to a  
thermoelectric conversion material having a novel  
structure and a manufacturing method thereof. More  
10 particularly, it relates to a novel structure of a  
thermoelectric conversion material that has a high  
thermoelectric figure of merit in a thermoelectric  
conversion device, which converts heat to electricity  
or converts electricity to heat, and also to a  
15 manufacturing method thereof.

## BACKGROUND ART

It is well known that if a thermoelectric  
conversion material, such as bismuth (Bi), bismuth  
20 telluride (BiTe) or silicon-germanium (SiGe), has a  
low dimensional structure, such as a superlattice  
structure or nano-wire structure (quantum wire  
structure), it will have a larger thermoelectric  
figure of merit  $Z$  than it would have in bulk form  
25 (Hicks, L.D., Dresselhaus, M.S., Phys. Rev. B., Vol.  
47, 12727(1993)). One main reason for this is that a  
low dimensional structure of the material provides a

quantum effect and increases the interface, which leads to a modified density of state and a modified phonon scattering without a substantial change in resistivity, resulting in a higher Seebeck

5 coefficient  $\alpha$  and a lower thermal conductivity than in a bulk material. In particular, a thermoelectric material in a nano-wire form has a largely modified density (i.e., increase in density at band edge) due to the quantum effect. Therefore, this material can

10 have a larger thermoelectric figure of merit than a two-dimension structure, such as a super-lattice structure.

The figure of merit  $Z$ , which is commonly used as an index of a thermoelectric material, is defined

15 as follows:

$$Z = \alpha^2 / \chi \rho \quad (1),$$

where  $\alpha$  represents a Seebeck coefficient;  $\chi$  represents a thermal conductivity;  $\rho$  represents a resistivity. As shown by the equation, an increase in

20 the Seebeck coefficient  $\alpha$  or a decrease in the thermal conductivity  $\chi$  leads to an increase in the figure of merit  $Z$ .

Accordingly, to increase the  $Z$  value, attempts have been made to produce various thermoelectric

25 materials (semiconductor materials) in a nano-wire form (quantum wire form). For example, an attempt has been made to produce a nano-wire of a thermoelectric

material, such as BiTe, BiSb or Bi, by filling pores in a porous oxide film formed by anodization of aluminum (anodized alumina) with this material (BiTe, BiSb or Bi) (Amy L. Prieto, Melissa S. Sander, Marisol S. Martin-Gonzalez, Ronald Gronsky, Timothy Sands, and Angelica M. Stacy "J. Am. Chem. Soc." Vol.123, 7160-7161(2001)).

The anodization of aluminum will now be briefly described. In an aluminum anodization process, an anodizing aluminum plate or aluminum film formed on a substrate in an electrolyte acid produces porous oxide film (anodized alumina) (RC. Furneaux, W. R. Rigby & A. P. Davidson "Nature" Vol. 337, P147 (1989)). The characteristic geometrical feature of the porous oxide film is that fine cylindrical pores several nanometers to several hundred nanometers (nano-holes) in diameter are arranged in parallel, spaced apart by several tens nanometers to several hundred nanometers (cell sizes). Cylindrical pores spaced apart by at least several tens of nanometers have a high aspect ratio and a relatively uniform cross-sectional diameter. The diameter and spacing of the pores can be controlled to a certain degree by properly selecting the acid species and the voltage for anodization.

Thus, such anodized aluminum oxide film can be used as a mold to produce a thermoelectric material

in a nano-wire form, which will increase the figure of merit  $Z$ .

However, in the anodization process of aluminum, when the anodization voltage is adjusted to form pores at spacing of 10 nm or less, so as to obtain nano-wires at a high density, it is difficult to form adjacent pores separated from each other by an anodized alumina wall 93 on a substrate 94 as shown in Fig. 9; i.e., pores tend to communicate with each other. In this situation, the anodized alumina 93 contains a greater number of non-isolated pores 92 than isolated pores 91. Thus, it is difficult to produce pores separated by alumina walls that are spaced apart by 10 nm or less, and a large area is required to produce a large number of nano-wires.

According to a theoretical calculation, the smaller the size (diameter) of the nano-wire, the greater the figure of merit  $Z$ . However, the anodization of aluminum can only produce pores or nanowires that are about 7 to 9 nm in size (diameter), and it is difficult to form pores of a cross-sectional size (or diameter) that is less than 7 nm. In other words, it is difficult to increase the figure of merit by producing nano-wires of a cross-sectional size (diameters) of 7 nm or less.

Accordingly, it is an object of the present invention to provide a thermoelectric conversion

material and a thermoelectric conversion device of a novel structure by forming nano-wires of a thermoelectric material that have a narrower size at a higher density than those conventionally fabricated,  
5 to increase the figure of merit  $Z$ .

It is also an object of the present invention to provide a manufacturing method to easily produce such a thermoelectric conversion material.

#### 10 DISCLOSURE OF THE INVENTION

A first aspect of the present invention is a thermoelectric conversion material having a multi-column structure, which comprises a porous body having columnar pores and a semiconductor material  
15 that can perform thermoelectric conversion, introduced into the pores of the porous body, characterized in that the porous body is formed by removing the material forming the columns from a structure in which a plurality of columns of a  
20 column-forming material containing a first component are distributed in a matrix containing a second component being eutectic with the first component.

A second aspect of the present invention is a thermoelectric conversion material having a multi-  
25 column structure, characterized in that the column structure is obtained by the steps of: providing a porous body having a plurality of columnar pores,

which porous body is formed by removing the material forming the columns from a structure in which a plurality of columns of a column-forming material containing a first component are distributed in a matrix containing a second component that is eutectic with the first component, introducing into the pores a semiconductor material that can perform thermoelectric conversion; and then removing the porous body.

10            Preferably, the porous body is a thin film.

          According to the present invention, it is possible to obtain nano-wires of a thermoelectric material having cross-sectional size and density that cannot be achieved by the conventional anodization of aluminum.

15            According to the present invention, it is possible to obtain a structure comprising a plurality of columns and a matrix surrounding the columns, wherein the columns have a Seebeck coefficient at a room temperature larger than when the material forming columns is in a bulk solid. The present invention also provides a thermoelectricity conversion device comprising, on a substrate, a structure, which comprises columns of a material and a matrix surrounding the columns, wherein the columns have a Seebeck coefficient larger than that of the material in a bulk solid at room temperature, and the

columns are electrically connected to electrodes; and the device generates current in response to external thermal change.

In the present invention, the porous body may  
5 be subjected to a chemical treatment before the semiconductor material is introduced into the pores. The chemical treatment is desirably an oxidation treatment. Such a chemical treatment (oxidation treatment) of the porous body allows the porous body  
10 to be chemically stabilized. In some cases, the chemical treatment (oxidation treatment) can decrease the thermal conductivity of the porous body to a level that is lower than that of anodized alumina, thereby increasing the efficiency of the resulting  
15 thermoelectric conversion device.

In the present invention, preferably, the column-forming material is aluminum; the matrix is silicon or germanium; and the structure has 20  
atomic% (inclusive) to 70 atomic% (inclusive) of  
20 silicon or germanium.

In the present invention, the main component of the porous body is silicon or germanium or a complex thereof, except for oxygen. Such a composition allows formation of nano-wires of a thermoelectric material,  
25 having density and cross-sectional size that cannot be achieved by the anodization of aluminum.

The cross-sectional size of a column in the

column-containing structure is desirably between 0.5 nm (inclusive) and 15 nm (inclusive). Such a cross-sectional pore size can provide a higher thermoelectric figure of merit.

5           The spacing of the columns in the column-containing structure is desirably between 5 nm (inclusive) and 20 nm (inclusive). Such spacing can provide higher density thermoelectric material nano-wires.

10           A part of the column-forming material is desirably a crystalline material, and the matrix is desirably made of an amorphous material.

          According to one aspect of the present invention, there is provided a manufacturing method  
15 of a thermoelectric conversion material of the present invention that comprises the steps of: providing a structure in which columns of a column-forming material containing a first component are distributed in a matrix containing a second component  
20 that is eutectic with the first component; removing the column-forming material from the structure to obtain a porous body; and introducing a semiconductor material into the pores of the porous body.

          The method may have a further step of removing  
25 the matrix after the introduction step. The method may also have a step of chemically treating the porous body after the removal step. The chemical



treatment is desirably an oxidation treatment. The removal step is desirably etching. The introduction step is, preferably, electrodeposition.

The semiconductor material is, typically, but  
5 not limited to, an alloy crystal composed of Bi, Sb, Te, and/or Se, such as BiSb or BiTe, and it may also be made from other various materials used as a thermoelectric conversion material in a bulk form, such as Si, SiGe, etc.

10 Investigating microstructures containing aluminum, the inventors of the present invention found that in the preparation of an aluminum film on a substrate by using a film deposition method in a non-equilibrium state, such as sputtering, when  
15 silicon and/or germanium are added in a predetermined ratio to aluminum, multiple aluminum columns are formed in silicon or germanium or a mixture thereof in a self-organizing manner. The inventers also found that when the film containing columnar aluminum is  
20 immersed in a solution that dissolves aluminum, but not silicon or germanium or a mixture thereof, a porous body can be produced having a fine cross-sectional size and high pore density that cannot be achieved by anodization of aluminum.

25 The inventers found that the oxidation treatment of the produced porous body can change the material constituting the porous body to an oxide

material.

The inventors carried out an intensive study on the basis of the above findings to complete the present invention.

5           It is essential to use an aluminum-silicon (germanium) film in which the ratio of silicon (or germanium) to the total of aluminum and silicon (or germanium) is between 20 and 70 atomic%, because a nano-structure having multiple columns of aluminum  
10 can be formed only in such a range. In other words, if the content of silicon (or germanium) is less than 20 atomic% of the total amount of aluminum and silicon (or germanium), the cross-sectional size of aluminum columns becomes 15 nm or more, while if the  
15 ratio of the amount of silicon (or germanium) to the sum amount of aluminum and silicon (or germanium) is more than 70 atomic%, an aluminum columnar structure cannot be identified by typical scanning electron microscopes.

20           Introducing a semiconductor material by electrodeposition into such a porous body composed of silicon (or silicon oxide) or germanium (or germanium oxide) can produce nano-wires with a small cross-sectional size (for example, not less than 0.5 nm and  
25 less than 15 nm) at a high density (for example, spacing not less than 5 nm and less than 20 nm). It should be noted that the silicon (or silicon oxide)

portion or the germanium (or germanium oxide) portion constituting the porous body may be removed after the formation of the nano-wires.

The structure from which the porous body is  
5 obtained (mother structure) will now be described.

The mother structure used in the present invention comprises a first component and second component, in which columns (column-forming material) containing the first component are surrounded by a  
10 matrix containing the second component. In this constitution, the mother structure desirably contains not less than 20 atomic% of the second component and less than 70 atomic% of the total of the first component and the second component.

15 The content, which is here referred to as the ratio of the amount of the second component to the sum of the first component and second component, is preferably between 25 atomic% (inclusive) and 65 atomic% (inclusive), and more preferably between 30  
20 atomic% (inclusive) and 60 atomic% (inclusive).

It should be noted that the term "column-forming material" or "columns" refers to substantially columnar forms, and the material may further contain the second component, and the matrix  
25 may further contain the first component. The column-forming material and the matrix surrounding it may contain small amounts of oxygen, argon, nitrogen

and/or hydrogen.

The ratio can be determined quantitatively by, for example, inductively coupled plasma emission spectroscopic analysis. The values of the ratio  
5 described above are in atomic%. The range between 20 atomic% (inclusive) and 70 atomic% (inclusive) corresponds to the range between 20.65 wt% (inclusive) and 70.84 wt% (inclusive), with the atomic weight of Al being 26.982 and the atomic  
10 weight of Si being 28.086.

The first and second components are preferably a combination of materials having a eutectic point in their phase diagram (so called eutectic materials). Specifically, the eutectic point is 300°C or higher,  
15 and preferably 400°C or higher. A preferable combination of the first and the second components may be a combination of Al (as the first component) and Si (as the second component), a combination of Al (as the first component) and Ge (as the second  
20 component), or a combination of Al (as the first component) and  $\text{Si}_x\text{Ge}_{1-x}$  ( $0 < x < 1$ ) (as the second component).

The cross-section of the column-forming material is circular or oval. In the structure, the  
25 columns are distributed in a matrix containing the second component. The cross-sectional sizes of the columns (for circular cross sections, diameters) can

be controlled as a function of the composition of the structure (or the content of the second component), and their average size is between 0.5 nm (inclusive) and 50 nm (inclusive), and preferably between 0.5 nm  
5 (inclusive) and 20 nm (inclusive), more preferably between 0.5 nm (inclusive) and 10 nm (inclusive). If the shape is oval or the like, the major axis is preferably in such ranges. Here, the "average size" is a size derived directly from, or through computer  
10 image processing of, actual picture images of columnar portions observed by SEM imaging (a range of about 100 nm by 70 nm). The lower limit of the average cross-sectional size for practical use is 1 nm or larger, or several nm or larger.

15       The center-to-center distance of the columns,  $2R$  is between 2 nm (inclusive) and 30 nm (inclusive), preferably between 5 nm (inclusive) and 20 nm (inclusive), and more preferably between 5 nm (inclusive) and 15 nm (inclusive). It should be noted  
20 that the lower limit of the center-to-center distance  $2R$  should be determined at least such that the columns have adequate spacing, so that they do not contact each other.

      The structure is preferably in the form of a  
25 film. In this case, the columns are distributed in a matrix containing the second component where the columns are substantially perpendicular to the film

plane. There is no specific limitation on the thickness of the film, and the thickness may be between 1 nm and 100  $\mu\text{m}$ . Considering processing time, etc., the practical thickness is between 1 nm and 50  $\mu\text{m}$ . Preferably, a film of 300 nm or thicker still has a column-containing structure.

The structure is preferably in the form of a film, and may be formed on a substrate. The substrate may be, but is not limited to, an insulator substrate, such as quartz glass, a semiconductor substrate, such as a silicon substrate, gallium arsenide substrate or indium phosphide substrate, or, if the structure can be formed on a metal substrate or a substrate (a support matrix), a flexible substrate (of polyimide, for example).

The structure can be fabricated using a film deposition method conducted under non-equilibrium conditions. Such a film deposition method is preferably sputtering, but any other film deposition method that can be used to form a material under any non-equilibrium conditions can be used, including resistance heating evaporation, electron-beam evaporation (EB evaporation) or ion plating.

In the case of sputtering, magnetron sputtering, RF sputtering, ECR sputtering or DC sputtering may be used. Also, film deposition is performed typically in an argon atmosphere with a pressure in a reactor on

the order of 0.01 Pa to 1 Pa. Two individual material targets, or a first material target and a second material target, may be used. Alternatively a material target that contains the first material and  
5 second material that are sintered at a predetermined ratio can be used.

The structure on a substrate is formed at a substrate temperature between 20°C (inclusive) and 300°C (inclusive), preferably between 20°C (inclusive)  
10 and 200°C (inclusive).

Removing the column-forming material from the structure (by wet etching or dry etching) produces a porous body that contains multiple columnar pores. The etching only has to selectively remove the  
15 column-forming material, and the etchant is preferably an acid, such as phosphoric acid, sulfuric acid, hydrochloric acid or nitric acid. The pores in the porous body produced by the removal are preferably isolated from each other or not connected  
20 to each other.

The method for fabricating the porous body from the structure desirably has: a step of providing the structure containing a first component and a second component, in which the column-forming material  
25 containing the first component is surrounded by a matrix containing the second component, and the content of the second component in the structure is

such that a ratio of the amount of the second component to the sum of the first component and second component is between 20 atomic% (inclusive) and 70 atomic% (inclusive); and a step of removing  
5 the column-forming material from the structure.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram of a thermoelectric conversion material according to the  
10 present invention;

Fig. 2 is a process flow chart of a manufacturing method of a thermoelectric conversion material of the present invention;

Fig. 3 is a process flow chart of another  
15 manufacturing method of a thermoelectric conversion material of the present invention;

Fig 4 illustrates a manufacturing method of a thermoelectric conversion material according to the present invention;

20 Fig. 5 is a schematic diagram of a thermal conversion material of Example 1;

Fig. 6 is a schematic diagram of a thermal conversion material of Example 2;

Fig. 7 is a schematic diagram of a thermal  
25 conversion material of Example 3;

Fig. 8 is a schematic diagram of an exemplary thermoelectric conversion device employing a



thermoelectric conversion material of the embodiments and examples of the present invention; and

Fig. 9 is an exemplary cross-section view of anodized alumina in the prior art with the pore  
5 spacing being 10 nm or less.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Embodiments of the thermoelectric conversion materials and manufacturing methods thereof according  
10 to the invention will now be described with reference to the accompanied drawings.

#### Structure of Thermoelectric Conversion Material

Fig. 1 is a schematic diagram of an exemplary thermoelectric conversion material according to the  
15 embodiment. In this example, a thermoelectric conversion material is shown in which quantum wires (hereinafter, referred to as nano-wires) of a thermoelectric material having cross-sectional sizes of several nm (nanometers) to several tens nm are  
20 formed in the pores on a substrate. In Fig. 1, reference numeral 11 refers to a film form of a thermoelectric conversion material; reference numeral 12 refers to a thermoelectric material formed as nano-wires constituting the thermoelectric conversion  
25 material 11 (hereinafter, referred to as the nano-wire(s) if necessary); reference numeral 13 refers to a substrate; and reference numeral 14 refers to a

porous body.

The nano-wires 12 are provided in the porous body 14. As shown in Fig. 1, the nano-wires 12 are separated from each other by the porous body 14, and  
5 are provided perpendicularly, or substantially perpendicularly, to the substrate 13. The shape of the nano-wires 12 is columnar, as shown in Fig. 1. The diameter of the nano-wires 12 (the average diameter of nano-wires 12 viewed from the film  
10 surface) is between 0.5 nm (inclusive) and 15 nm (not inclusive), and the spacing of the nano-wires 12 (the average center-to-center distance of the nano-wires viewed from the film surface) is between 5 nm (inclusive) and 20 nm (not inclusive).

15 The porous body 14 constituting the thermoelectric conversion material 11 is formed by removing the column-forming material containing a first component distributed in a matrix containing a second component, which is eutectic with the first  
20 component. The column-forming material containing the first component consists, for example, of a material that contains aluminum as the main component. The matrix containing the second component, which is eutectic with the first component, for example, is  
25 germanium or silicon or a mixture of germanium and silicon.

The material of the porous body 14 preferably

contains silicon (or silicon oxide) or germanium (or germanium oxide) as the main component. Alternatively, it may contain a mixture of silicon and germanium (or oxide of the mixture) as the main component. The  
5 material of the porous body 14 desirably contains silicon or germanium (or oxide thereof) as the main component, and may contain several to several tens atomic% of aluminum (Al), argon (Ar), nitrogen (N) and/or hydrogen (H).

10 While the material of the porous body 14 is preferably amorphous, it may contain a crystalline material.

The material constituting the nano-wires is typically an alloy crystal consisting of Bi, Sb, Te  
15 and/or Se, such as Bi, BiSb or BiTe, but it is not limited thereto. Rather, it may be any one of various materials that are conventionally used as a thermoelectric conversion material in bulk form.

In Fig. 1, the thermoelectric material 11 is  
20 not limited to the above-described configuration. Its configuration may be formed after removing the porous body 14 separating the thermoelectric material 12.

Manufacturing Method of Thermoelectric Conversion Material

25 Manufacturing methods of the thermoelectric conversion material according to the present invention are described below.

Fig. 2 is a process flow chart of an embodiment of a thermoelectric conversion material manufacturing method. The manufacturing method shown in Fig. 2 has steps (a) to (c) as follows:

5           (a) a step of providing a structure in which columns of a material containing a first component are distributed in a matrix containing a second component, which is eutectic with the first component; then

10           (b) a step of removing the column-forming material from the structure to obtain a porous body; and then

            (c) a step of introducing a semiconductor material into the pores of the porous body.

15           Fig. 3 is a process flow chart of another embodiment of a method for manufacturing the thermoelectric conversion material:

            (a) a step of providing a structure in which columns of a material containing a first component  
20           are distributed in a matrix containing a second component, which is eutectic with the first component; then

            (b) a step of removing the column-forming material from the structure to obtain a porous body;

25           (c) a step of chemically treating (for example, oxidizing) the porous body; and then

            (d) a step of introducing a semiconductor

material into the pores of the porous body.

A manufacturing method of the thermoelectric conversion material will now be described more specifically with reference to the drawings.

5        Fig. 4 illustrates an exemplary manufacturing process of a thermoelectric conversion material of this embodiment. Steps (a) to (c) are described one by one.

Step (a): A structure in which columns of a  
10 material containing a first component 41 are distributed in a matrix containing a second component 44, which can be eutectic with the first component 41, is provided.

Here, for example, aluminum (first component  
15 41) and silicon (or germanium) (second component 44) are provided to form columns in a matrix. Then, a structured film of a mixture 43 (aluminum-silicon mixture film or aluminum-germanium mixture film) is formed on a substrate 42 by using a method such as  
20 sputtering that can produce a film in a non-equilibrium state.

When an aluminum-silicon mixture film (or aluminum-germanium mixture film) 43 is formed by using such a method, the aluminum and silicon (or  
25 germanium) form a eutectic structure in a meta-stable state in which the aluminum component separates and forms a nano-structure containing multi-columns of

several nm in the matrix in a self-organizing manner. Such aluminum columns are in a shape of a circular cylinder with a diameter between 0.5 nm (inclusive) and 15 nm (not inclusive), and the column spacing is  
5 between 5 nm (inclusive) and 20 nm (not inclusive).

The silicon (or germanium) content in the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43 is in a range of 20-70 atomic% of the total content of aluminum and silicon (or  
10 germanium) in the film, preferably between 25 and 65 atomic%, and more preferably between 30 and 60 atomic %. Silicon content in such a range allows formation of the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43 in which columnar  
15 aluminum is distributed in a matrix of silicon (or germanium).

Here, the ratio of silicon to aluminum is represented by "atomic%" (atom% or at%), i.e., a ratio of the number of silicon (or germanium) atoms  
20 to that of aluminum. Such a ratio is obtained by a quantitative analysis of silicon (or germanium) and aluminum in the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43, for example, by using inductively coupled plasma emission  
25 spectroscopic analysis (ICP).

Step (b): Then, the column-forming material is removed.

Here, for example, aluminum, the column-forming material in the aluminum-silicon mixture film (or aluminum-germanium mixture film) 43, is etched away with phosphoric acid to form pores 46 in the matrix  
5 (here, silicon or germanium). This produces a porous body 45 on the substrate 42.

The pores 46 in the porous body 45 have a spacing from 5 nm (inclusive) to 20 nm (not inclusive) and their cross-sectional size is from 0.5  
10 nm (inclusive) to 15 nm (not inclusive).

The etching solution can be a solution of an acid, such as phosphoric acid, sulfuric acid, hydrochloric acid or chromic acid, which dissolves aluminum, but hardly dissolves silicon or germanium.  
15 However, it may be an alkaline solution, such as an aqueous sodium hydroxide, as long as it does not have an adverse effect on the pore formation by etching. Thus, the etching solution should not be limited to specific types of acid or alkali. A mixture of acid  
20 solutions or alkaline solutions may also be used. The etching conditions, such as solution temperature, concentration and time, can be selected in a suitable manner depending on the porous body to be produced.

Step (c): A thermoelectric material  
25 (semiconductor material) 47 is introduced into the pores of the porous body produced by the removal step. Thus, the thermoelectric material 47 becomes nano-

wires.

In this step, the porous body is filled with the thermoelectric material 47. For example, Bi or BiTe is filled into the pores by electrodeposition.

5 The thermoelectric material 47 is typically BiSb or BiTe, which inherently has a high thermoelectric figure of merit. However, the material should not be so limited, and various other materials that are used as thermoelectric conversion materials in bulk form  
10 may be employed.

The method for filling the pores with the material is preferably electrodeposition. The pores may also be filled using a catalytic reaction method or VLS.

#### 15 Configuration of Thermoelectric Conversion Device

Fig. 8 is a schematic diagram of an exemplary thermoelectric conversion device of this embodiment. Here, the "thermoelectric conversion device" is either a thermoelectric generating device that  
20 converts heat to electricity, or a thermoelectric cooling device that provides a cooling effect by the current flowing therethrough. Fig. 8 shows an example of such a thermoelectric generating device. The thermoelectric generating device of the present  
25 invention comprises a section of p-type thermoelectric conversion material 103 and a section of n-type thermoelectric conversion material 105.



Either thermoelectric conversion material section comprises a plurality of nano-wires (102 or 104) and a porous body 101. Fig. 8 shows only a pair of a p-type thermoelectric conversion material section 103  
5 and an n-type thermoelectric conversion material section 105. However, a typical configuration of the device has a plurality of such pairs arranged in series.

Here, a higher temperature electrode 108 and  
10 lower temperature electrodes 107 and 106 are not supported on support plates. However typical electrodes are desirably supported on a support plate.

#### Examples

The present invention will now be described by  
15 providing specific examples.

#### Example 1

In this example, a thermoelectric conversion material was produced, in which the porous body having columnar pores was amorphous silicon, and the  
20 semiconductor filled into the pores was BiTe.

First, an aluminum-silicon mixture film about 200 nm thick containing 37 atomic% of silicon to the total of aluminum and silicon was formed by magnetron sputtering on a silicon substrate, on which 20 nm of  
25 tungsten was deposited as an electrode for electrodeposition of BiTe (thermoelectric material). As a target, six 15-mm square silicon chips are

placed on a circular aluminum target of 4 inches in diameter (101.6 mm). Sputtering conditions employed were such that a supply was used with an Ar flow of 50 sccm, a discharging pressure of 0.7 Pa and input  
5 power of 1 kW. The substrate temperature was room temperature (25°C).

The aluminum-silicon mixture film thus obtained was observed by an FE-SEM (Field Emission-Scanning Electron Microscope). When the surface was viewed  
10 from above at an angle, it was found that round aluminum columns surrounded by the silicon matrix were arranged two-dimensionally, as shown in (a) of Fig. 4. The diameter of the aluminum column-forming material was 5 nm, and the average column spacing  
15 (center-to-center distance) was 8 nm. The FE-SEM observation of the cross-section shows that the aluminum columns were isolated from each other.

Then, the aluminum-silicon mixture film thus fabricated was immersed in 98% concentrated sulfuric  
20 acid for 24 hours to selectively etch away only the aluminum column-forming material so that pores were formed. As a result, a porous body was produced that consists of a material containing silicon as the main component, except for oxygen. The surface of the  
25 pores was oxidized.

The porous body consisting of a matrix containing silicon as the main component (the

aluminum-silicon mixture film that had been subjected to the etching with concentrated sulfuric acid) was observed by the FE-SEM. The surface viewed from above at an angle had pores surrounded by the silicon  
5 matrix, arranged two-dimensionally, as shown in (b) of Fig. 4. The diameter of the pores was 5 nm, and the average spacing of the pores was 8 nm.

Then, BiTe (semiconductor material) was filled into the pores of the porous body containing silicon  
10 as the main component. Here, a solution of 1 mol/l nitric acid dissolving Bi and Te therein was used for the electrodeposition of BiTe. The electrodeposition was performed in the solution with an Ag/AgCl reference electrode at -1.0 V. Then, BiTe protruding  
15 from the pores was polished away.

The BiTe nano-wires thus fabricated in the porous body were observed with the FE-SEM to show that the substrate surface viewed from above at an angle had BiTe nano-wires 57 arranged two-  
20 dimensionally surrounded by the porous body 54 consisting of silicon as the main component, in a thermoelectric conversion material 53 formed on the substrate 52 shown in Fig. 5. The nano-wires 57 were observed in a cross-section to have a columnar form.  
25 The average diameter of the nano-wires 57 was 5 nm, and the average center-to-center distance of the adjacent nano-wires 57 was about 8 nm.

## Example 2

In this example, a thermoelectric conversion material was produced, in which the main component of the porous body having the columnar pores was silicon oxide, and the semiconductor filled into the pores was BiTe.

First, an aluminum-silicon mixture film about 200 nm thick containing 37 atomic% of silicon to the total of aluminum and silicon was formed by magnetron sputtering on a silicon substrate, on which 20 nm of tungsten was deposited as an electrode for electrodeposition of BiTe (thermoelectric material). As a target, six 15-mm square silicon chips are placed on a circular aluminum target of 4 inches in diameter (101.6 mm). Sputtering conditions employed were such that a supply was used with an Ar flow of 50 sccm, a discharging pressure of 0.7 Pa and input power of 1 kW. The substrate temperature was room temperature (25°C).

The aluminum-silicon mixture film thus obtained was observed with an FE-SEM (Field Emission-Scanning Electron Microscope) to find that the substrate surface viewed from above at an angle had a feature in which round aluminum columns surrounded by the silicon matrix were arranged two-dimensionally, as shown in (a) of Fig. 4. The diameter of the column-forming aluminum material was 5 nm, and the average

spacing (center-to-center distance) of the columns was 8 nm. The FE-SEM observation of the cross-section showed that the aluminum columns were isolated from each other.

5           Then, the aluminum-silicon mixture film thus fabricated was immersed in 5wt% phosphoric acid for 7 hours to selectively etch away only the aluminum column-forming material so that pores were formed. At that point, the silicon matrix that surrounded the  
10 aluminum columns was oxidized. As a result, a porous body was produced consisting of a material containing silicon oxide as the main component.

          The porous body mainly consisting of silicon oxide was observed by the FE-SEM. The surface viewed  
15 from above at an angle had pores surrounded by the silicon oxide matrix, arranged two-dimensionally, as shown in (b) of Fig. 4. The diameter of the pores was 5 nm, and the average spacing of the pores was 8 nm. The FE-SEM observation of the cross-section showed  
20 that the pores were isolated from each other by the matrix mainly consisting of silicon oxide.

          Then, BiTe (semiconductor material) was filled into the pores of the porous body containing silicon oxide as the main component. Here, a solution of 1  
25 mol/l nitric acid dissolving Bi and Te therein was used for the electrodeposition of BiTe. The electrodeposition was performed in the solution with

a reference electrode of Ag/AgCl at -1.0 V. Then, BiTe protruding from the pores was polished away.

The BiTe nano-wires thus fabricated in the porous body were observed by the FE-SEM. When the surface of a thermoelectric conversion material formed on the substrate was viewed from above at an angle, it was shown that BiTe nano-wires were arranged two-dimensionally surrounded by the porous body consisting of silicon oxide as the main component, as shown in Fig. 6. The nano-wires were observed to have a columnar shape. The average diameter of the nano-wires was 4 nm, and the average center-to-center distance of the adjacent nano-wires was about 8 nm.

### Example 3

In this example, a thermoelectric conversion material was produced, in which the material of the porous body having the columnar pores was germanium, and the semiconductor filled into the pores was BiSb.

First, an aluminum-germanium mixture film of about 200 nm that contained 37 atomic% of germanium relative to the sum amount of aluminum and germanium was formed by magnetron sputtering on a silicon substrate, on which tungsten of 20 nm thick had been deposited as the electrode for electrodeposition of BiSb (thermoelectric material). A target was used in which four 15-mm square germanium chips are placed on

a circular aluminum target having a diameter of 4 inches (101.6 mm). Sputtering conditions were employed where RF power supply was used with an Ar flow: 12 sccm, a discharging pressure: 0.05 Pa and  
5 input power: 60 W. The substrate temperature was room temperature (25°C).

The aluminum-germanium mixture film thus obtained was observed with the FE-SEM, and it was then found that the substrate surface viewed from an  
10 upper side with a slant had a feature in which substantially circular column-forming aluminum material was arranged two-dimensionally while surrounded by the germanium matrix, as shown in (a) of Fig. 4. The diameter of the aluminum columns was  
15 10 nm, and the average center-to-center distance of the columns was 15 nm.

Then, the aluminum-germanium mixture film that contained 37 atomic% of germanium relative to the sum amount of aluminum and germanium was immersed in 98%  
20 concentrated sulfuric acid for 24 hours to selectively etch away only the aluminum column-forming material so that pores were formed. As a result, a porous body was produced containing germanium as the main component.

25 The aluminum-germanium mixture film that had been etched with a concentrated sulfuric acid (the porous body consisting of material containing

germanium as the main component) was observed by the FE-SEM, and it was then found that the substrate surface viewed from an upper side with a slant had a feature in which pores were arranged two-  
5 dimensionally while surrounded by the germanium matrix, as shown in (b) of Fig. 4. The diameter of the pores,  $2r$ , was 10 nm, and the average spacing of the pores was 15 nm. Thus, the porous body containing germanium as the main component was produced. The  
10 fabricated sample was subjected to X-ray diffraction analysis and found to be amorphous.

Then, a semiconductor material was filled into the porous body thus produced containing germanium as the main component. Here, BiSb was filled into the  
15 porous body to produce BiSb nano-wires in the porous body. Electrodeposition of BiSb was employed with a solution of dimethyl sulfoxide (DMSO) in which  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{SbCl}_3$  were dissolved. The electrodeposition was performed in the solution with  
20 an Ag/AgCl reference electrode at -1.0 V. Then, the BiSb portions protruding from the pores were polished away.

The BiSb nano-wires thus fabricated formed in the porous body were observed by the FE-SEM, and it  
25 was then found that the surface viewed from an upper side with a slant had a feature in which BiSb nano-wires 77 were arranged two-dimensionally while



surrounded by the porous body 74 containing germanium as the main component, in a thermoelectric conversion material 73 formed on the substrate 72 shown in Fig. 7. Viewed from a cross-section of the substrate, the  
5 nano-wire 77 had a columnar form. The average diameter of the nano-wires 77 was 10 nm, and the average center-to-center distance of the adjacent nano-wires 77 was about 15 nm.

As described in the above examples, according  
10 to the present invention, when a semiconductor material (thermoelectric material) is filled into a porous body, which is formed by providing a structure in which columns of a material containing a first component are distributed in a matrix containing a  
15 second component that can be eutectic with the first component, and then the column-forming material is removed from the structure, thermoelectric material nano-wires with a diameter between 0.5 nm (inclusive) and 15 nm (not inclusive) and high density (the  
20 center-to-center distance of the nano-wires less than 20 nm) can be formed.

The material constituting the porous body may be any one of the various materials, such as silicon or germanium.

#### 25 Example 4

In this example, a thermoelectric generating device was produced in which BiTe was employed as an

n-type thermoelectric material and BiSb was used as a p-type thermoelectric material.

First, an aluminum-silicon mixture film of about 2  $\mu\text{m}$  that contained 50 atomic% of silicon  
5 relative to the sum amount of aluminum and silicon was formed by magnetron sputtering on a silicon substrate having silicon oxide surface (a support plate), on which 20 nm of tungsten had been deposited. Then, the aluminum-silicon mixture film that  
10 contained 50 atomic% of silicon relative to the sum amount of aluminum and silicon was immersed in 5 wt% phosphoric acid for 8 hours to selectively etch only the aluminum column-forming material so that pores were formed. As the result, a porous body was  
15 produced that consists of material containing silicon oxide as the main component. Then, BiTe (n-type thermoelectric material) was electrodeposited. Then, resist patterns were formed by photolithography, and the n-type thermoelectric conversion material  
20 patterns were generated by dry etching. Using similar process steps, BiSb (p-type thermoelectric material) was electrodeposited on the porous body and the silicon substrate with silicon oxide (a support plate) with 20 nm of tungsten deposited thereon;  
25 resist patterns were formed by photolithography; and the p-type thermoelectric conversion material patterns were generated by dry etching. The silicon

substrate with silicon oxide, on which the p-type thermoelectric material is formed, and the silicon substrate with silicon oxide, on which the n-type thermoelectric material is formed, are attached  
5 together to form a thermoelectric conversion device, as shown in Fig. 8.

A thermoelectric conversion material employing a thermoelectric conversion material obtained by the above embodiments and examples will be described with  
10 reference to Fig. 8. A thermoelectric conversion device shown in Fig. 8, like known thermoelectric conversion devices in bulk form, is used for: a device, such as a cooler or thermal controller, which performs both cooling and heating where current  
15 flowing through a material causes heat generation at one end of the material and heat absorption at the other end, because of a Peltier effect; and a device, such as thermoelectric generator, which generates an electromotive force (thermoelectromotive force) by  
20 providing a temperature difference across a material (this is the opposite effect to that of the one mentioned above).

In Fig. 8, the thermoelectric conversion device is embodied as a unit composed of multiple devices  
25 ( $\pi$ -type devices) connected in series, with each  $\pi$ -type device consisting of: a thermoelectric conversion material section 103 having nano-wires 102

of a p-type semiconductor material (thermoelectric material) formed in a porous body 101 (hereinafter, referred to as a "p-type material section" 103); and a thermoelectric conversion material section 105  
5 having nano-wires 104 of an n-type semiconductor material (thermoelectric material) formed in a porous body 101 (hereinafter, referred to as an "n-type material section") 105. In Fig. 8, reference numeral 106 refers to an electrode provided on one end of the  
10 p-type material section 103 (hereinafter, referred to as lower temperature-side); reference numeral 107 refers to an electrode provided on one end of the n-type material section 105 (hereinafter, referred to as lower temperature-side); and reference numeral 108  
15 refers to an electrode provided on the other ends of the material sections 103 and 105.

In the case where the thermoelectric conversion device is used as a thermoelectric generating device, a plurality of the  $\Pi$ -type devices of Fig. 8 are  
20 connected in series. The temperature difference between the upper electrode 108 and the lower electrodes 106 and 107 can cause the generation of electric power. In Fig. 8, the upper electrode 108 is at a higher temperature while the lower electrodes is  
25 at a lower temperature, thereby generating an electromotive force between the lower electrodes 106 and 107, with the lower electrode 106 being positive

and the lower electrode 107 being negative. The thermoelectric conversion device can also be used as a cooling device, in which the electrode 106 is connected to a negative terminal of a power supply and the electrode 107 is connected to a positive terminal of the power supply, and current flowing therethrough can cause heat absorption from the upper electrode 108 in Fig. 8. Thus, cooling around the upper electrode 108 can be performed. Such a thermoelectric conversion device can have a higher thermoelectric conversion figure of merit  $Z$  than conventional thermoelectric conversion devices.

The present invention is not limited the embodiments, examples and applications illustrated above, but those skilled in the art can vary and modify them based on the claims without departing from the gist of the present invention. Such variations and modifications are also within the scope of the present invention.

As described in the above examples, according to the present invention, when a semiconductor material (thermoelectric material) is filled into a porous body, which is formed by providing a structure in which columns of a material containing a first component are distributed in a matrix containing a second component that can be a eutectic with the first component, and then removing the column-forming

material from the structure, nano-wires of thermoelectric material with a diameter between 0.5 nm (inclusive) and 15 nm (not inclusive) and high density (the spacing of the nano-wires less than 20  
5 nm) can be formed. An apparatus employing such a thermoelectric conversion device can also be provided. The present invention can also provide a method that allows an easy production of the thermoelectric conversion device.

## ABSTRACT

A thermoelectric conversion material and a thermoelectric conversion device having a novel structure with an increased figure of merit are provided by forming nano-wires of thermoelectric material in a smaller cross-sectional size. The thermoelectric conversion material comprises nano-wires obtained by introducing a thermoelectric material (semiconductor material) into columnar pores of a porous body. The porous body is formed by providing a structure in which columns of a column-forming material containing a first component (for example, aluminum) are distributed in a matrix containing a second component (for example, silicon or germanium or a mixture of them) being eutectic with the first component, and then removing the column-forming material from the structure. The average diameter of the nano-wires of the thermoelectric material is 0.5 nm or more and less than 15 nm, and the spacing of the nano-wires is 5 nm or more and less than 20 nm.